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SEMICONDUCTOR GRADE, SOLAR SILICON PURIFICATION PROJECT

Motorola Report No. 2257/6

Technical Quarterly Report No. 6

JPL CONTRACT NO. 954442

By

William M. Ingle

Principal Investigator

Robert Chaney and Stephen Thompson

Period Covered: 1 April 1977 - 30 June 1977

Date Issued: 25 July 1977

PREPARED BY

MOTOROLA INC. SEMICONDUCTOR GROUP  
5005 E. McDowell Road  
Phoenix, Arizona 85005



This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U. S. Energy Research and Development Administration, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

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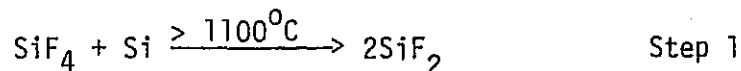
## ABSTRACT

An investigation has been undertaken to examine the potential for a three step  $\text{SiF}_2$  polymer transport purification process. The process involves reacting low cost mg silicon with  $\text{SiF}_4$  to yield  $\text{SiF}_2$  gas which is condensed to form polymeric  $(\text{SiF}_2)_x$ . The polymer is then heated above  $400^\circ\text{C}$  to yield Si,  $\text{SiF}_4$  and higher  $\text{Si}_n\text{F}_{2n+2}$  homologues.

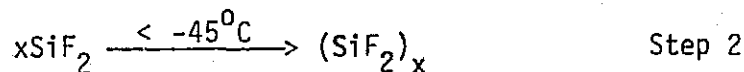
This report presents and discusses continuing progress on (i) observations on  $(\text{SiF}_2)_x$  polymer formation and depolymerization on the small coil, (ii) mass balance studies, (iii) partial pressures of  $\text{SiF}_2$  and  $\text{SiF}_4$ , (iv)  $\text{AlF}_3$  mass spectral studies, and (v) material analysis studies.

## I INTRODUCTION

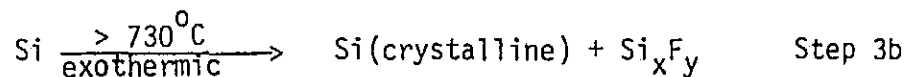
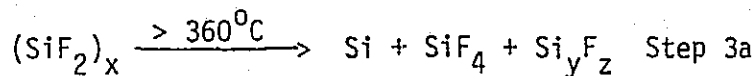
The purpose of the present investigation is to convert metallurgical grade silicon (mg Si) into semiconductor grade silicon (sg Si) via a 3 step  $\text{SiF}_2$  polymer transport purification process. The first step<sup>1</sup> involves the reaction of  $\text{SiF}_4$  with mg Si to yield gaseous  $\text{SiF}_2$ .



This is followed by a polymer formation step.<sup>2</sup>



Finally, the polymer is converted into high purity silicon,  $\text{SiF}_4$  and higher homologues.<sup>3</sup>



The mg Si undergoes purification in all three steps of the above transport processes.

Progress is reported on the project in five major areas. These are:

- i) Observations on  $(\text{SiF}_2)_x$  polymer formation and conversion on the small coil
- ii) Mass balance studies
- iii) Partial pressures of  $\text{SiF}_2$  and  $\text{SiF}_4$
- iv)  $\text{AlF}_3$  mass spectral studies
- v) Material analysis studies.

Finally, conclusions on current results will be presented in conjunction with recommendations for future work.

## II EXPERIMENTAL

### A. Equipment Modification

#### 1. Modifications of the Kinetic and Rate Apparatus to Optimize Polymer Conversion

Modification of the 2" reactor has taken place in order to study the condensation and conversion of the polymer into silicon.

The apparatus used consisted of the small 2 inch coil reactor previously described<sup>4</sup>, fitted with a condensation disproportionation coil (hereafter termed C-D coil) depicted in Figure 1a and 1b.

The C-D coil consists of a helical spiral of 0.5 inch quartz tubing with gaseous inlet and outlet facilities fixed inside a 2 inch diameter quartz column (Figure 1b).

A high temperature, high resistance alumel wire is fixed inside the quartz spiral with electrical connections made to two 140 V/12 A Variac transformers connected in series. Apertures at inlet and outlet ports allow insertion of thermocouples for temperature monitoring, (Figure 1b).

Operation of the coil involves passage of liquid nitrogen through the inner quartz helix facilitating condensation of gaseous  $\text{SiF}_2$  into polymer  $(\text{SiF}_2)_x$ . Temperatures on the helix as low as  $-180^\circ\text{C}$  have been achieved by this technique. Subsequent to condensation of  $(\text{SiF}_2)_x$  upon the coil, conversion of the polymer (reaction step 3) is brought about by passing an electrical current through the wire running down the center of the helix. This causes the wire to heat, resulting in conversion of the polymer adhering to the coil. It has been found that better heat transfer to the coil can be achieved when helium is passed down the spiral as the wire is heated. Temperatures as high as  $550^\circ\text{C}$  have been obtained via this technique.



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Figure 1(a)

36 inch quartz C-D coil

(1) inlet/out/electrical  
connection apperture

(2) quartz spiral

(3) trap

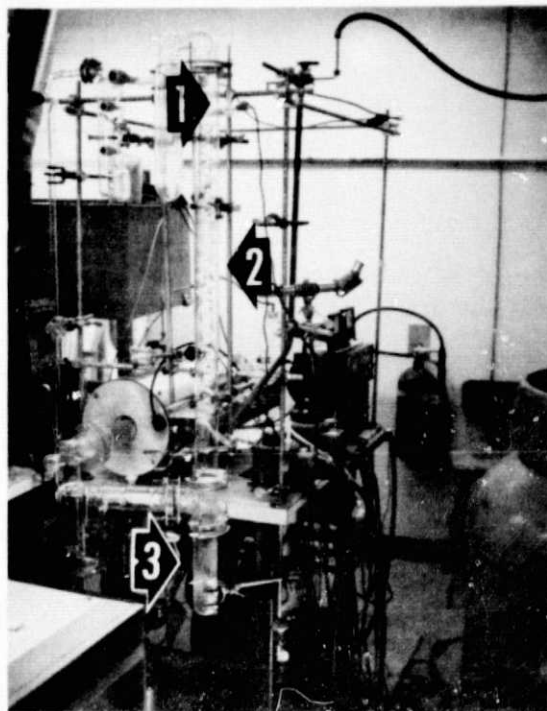


Figure 1(b)

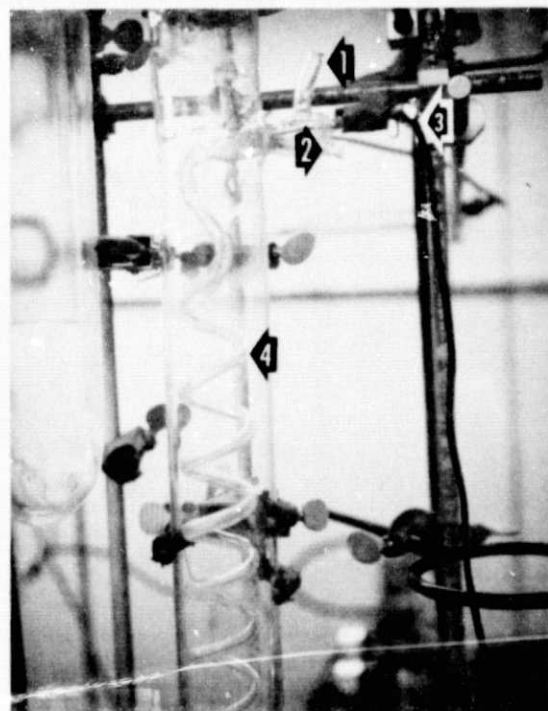
Close up of 36 inch quartz C-D coil

(1)  $N_2/He$  inlet/outlet

(2) Thermocouple aperture

(3) Electrical connection

(4) Alumel heating wire inside  
quartz spiral



The most effective procedure for achieving temperatures between  $0^{\circ}\text{C}$  and  $-100^{\circ}\text{C}$  involved heating the wire concurrent while passing liquid  $\text{N}_2$  down the spiral. Temperatures constant to  $\pm 1^{\circ}\text{C}$  have been obtained with this method.

## 2. Construction of Second Small Vacuum Furnace for Polymer Conversion Experiments

A second small vacuum furnace is presently being assembled. It will be used to determine temperature and residence times necessary for conversion of the  $\text{Si}_n\text{F}_{2n+2}$  homologues into Si and  $\text{SiF}_4$ . Specifically, in the conversion of  $(\text{SiF}_2)_x$  polymer into Si and  $\text{SiF}_4$  we have recently observed that the major route for the conversion is via  $\text{Si}_n\text{F}_{2n+2}$  homologues of intermediate molecular weight. While in this state, the homologues apparently undergo thermal rearrangement to yield the more thermally stable branched chain isomers.<sup>5</sup> Thus, these studies will determine the conditions necessary for optimum  $\text{Si}_n\text{F}_{2n+2}$  homologue conversion.

### B. Partial Pressures of Reactants and Products

Calculations have been performed utilizing data<sup>6</sup> obtained from the mg Si and  $\text{SiF}_4$  reaction at  $1350^{\circ}\text{C}$  to correlate partial pressures of reactants and products with  $\text{SiF}_2$  and  $\text{SiF}_4$  counts. The silicon charge consisted of particle sizes of 0.1 cm to 2 cm packed in a quartz reaction tube as previously described.<sup>4</sup>  $\text{SiF}_4$  was 99.6% pure supplied by Synthatron Company.

The downstream total pressure was monitored by three thermocouple pressure gauges. The concentration of  $\text{SiF}_2$  and  $\text{SiF}_4$  in the gas stream emerging from the reaction chamber was monitored by the Finnigan GC/MS data system in the EI source mode at 19.5 eV.

### III RESULTS AND DISCUSSION

#### A. Mass Balance Studies

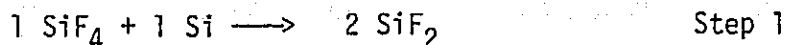
In order to derive information regarding the  $\text{SiF}_2$  concentration under specified reaction conditions and to examine the reliability of the ratio of  $\text{SiF}_2$  to  $\text{SiF}_4$ , a series of mass balance experiments has been undertaken.

In conjunction with these studies, data regarding the stoichiometry has been collected.

A prerequisite to accurate mass balance determination is precise knowledge of the weight of  $\text{SiF}_4$  delivered by the mass flow controller with time. Due to the corrosive nature of  $\text{SiF}_4$ , an accurate calibration of the Matheson flow controller was performed for flows between 12.5 and 200 sccm. Matheson reports a gas conversion factor for their flow controller of 0.394 for  $\text{SiF}_4$  based on the specific heat of air and the specific heat of  $\text{SiF}_4$  at  $21^\circ\text{C}$ .<sup>47</sup> A value of  $0.51 \pm 0.01$  has been obtained in our calibration experiments using a  $\text{SiF}_4$  flow of 100 sccm, under our laboratory conditions.

Use of this conversion factor allows accurate calculation of the number of moles  $\text{SiF}_4$  delivered. Procedures have been developed to recover unreacted  $\text{SiF}_4$  which are accurate to within  $\pm 0.01$  gms at  $25^\circ\text{C}$ . Hence a knowledge of the weight of polymer recovered coupled with the weight of silicon consumed during the reaction will provide information for (i) accurate mass balance calculations, (ii) correlation of counts to actual weight of reactants and products, and (iii) stoichiometric determination of reaction 1.

Experiments conducted at  $1350^\circ\text{C}$  show that  $\sim 75\%$  of the reactant  $\text{SiF}_4$  is consumed in the reaction. Furthermore, a stoichiometry for reaction step 1,  $x \text{ SiF}_4 + y \text{ Si} \longrightarrow z \text{ SiF}_2$ , has been determined to be exactly



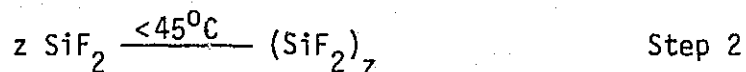
at  $1350^\circ\text{C}$ . (Table I).

TABLE I

Stoichiometry of reaction step 1

$$\begin{aligned} x &= 6.82 \cdot 10^{-2} \text{ moles SiF}_4 \text{ reacted} \\ y &= 6.6 \cdot 10^{-2} \text{ moles Si reacted} \\ z &= 1.35 \cdot 10^{-1} \text{ moles SiF}_2 \text{ produced} \end{aligned}$$

These stoichiometric experiments involved weighing the unconverted polymer produced and the assumption that formation of the polymer followed reaction step 2.<sup>3</sup>



Mass balance results for reaction step 1 are such that total weight products/total weight reactants differ by less than 1%.

$$\frac{\sum \text{products}}{\sum \text{reactants}} \geq 0.99$$

It is concluded from the stoichiometry, percent SiF<sub>4</sub> conversion and mass balance experiments that reaction step 1 is correct as written using Motorola's experimental apparatus and procedure. Further, a 75% conversion of SiF<sub>4</sub> has been obtained, a considerable increase over previous workers. (Table II).

TABLE II

	<u>% SiF<sub>4</sub> Conversion</u>	<u>Ref.</u>
Pease	40%	2
Margrave	48%*	3
Motorola	75%	this work

Data correlating GC/MS counts and partial pressures of reactants and products have been evaluated; experiments involving the 2 inch proto-type coil reactor have been undertaken.

\* Calculation based on reference 3.

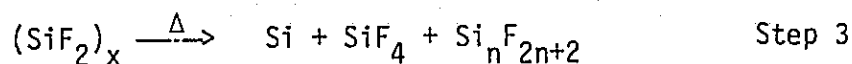
### B. Partial Pressures of SiF<sub>2</sub> and SiF<sub>4</sub> in the Gas Stream

While the ratio of SiF<sub>2</sub>/SiF<sub>4</sub> counts in the gas stream provides insight into the conditions leading to maximum formation of product from reactants, the partial pressures of the reactants and products in the gas stream are also of interest. Consequently effort was focused at correlating the counts of SiF<sub>2</sub> and SiF<sub>4</sub> under given reaction conditions with the partial pressure of SiF<sub>2</sub> and SiF<sub>4</sub> in the gas stream. This calculation was based on the following data (1) the total downstream pressure measured, (2) the mole fraction of SiF<sub>2</sub> and SiF<sub>4</sub> derived from an accurate mass balance (3) the observed stoichiometry and (4) the counts of SiF<sub>2</sub> and SiF<sub>4</sub> measured by the GC/MS for the 1200 spectra comprising the mg Si + SiF<sub>4</sub> reaction at 1350°C and 1250°C. Two assumptions were made to allow the conversion from counts to partial pressures (1) that 99% of the downstream gas mixture was SiF<sub>2</sub> and SiF<sub>4</sub><sup>3</sup>, (2) that the polymer formation followed reaction step 2.

Figure 2 is a graph of the calculated downstream partial pressure of SiF<sub>2</sub> and SiF<sub>4</sub> versus SiF<sub>4</sub> flow into the reaction chamber for mg Si at 1350°C for flows up to the maximum measured 1.2 gms SiF<sub>4</sub>/minute.

### C. Preliminary Experiments Involving Polymer Conversion

Subsequent to the analysis of stoichiometry, mass balance and chemical feasibility of reaction step 1, a series of experiments has been undertaken to study the conversion of polymer into product via reaction step 3.



Three sets of experiments involving polymer conversion have been performed using the C-D coil. The first involved low temperature (-175°C) condensation of (SiF<sub>2</sub>)<sub>x</sub> on the C-D coil utilizing reaction conditions found in previous experiments to optimize SiF<sub>2</sub> production.<sup>4</sup> The second set

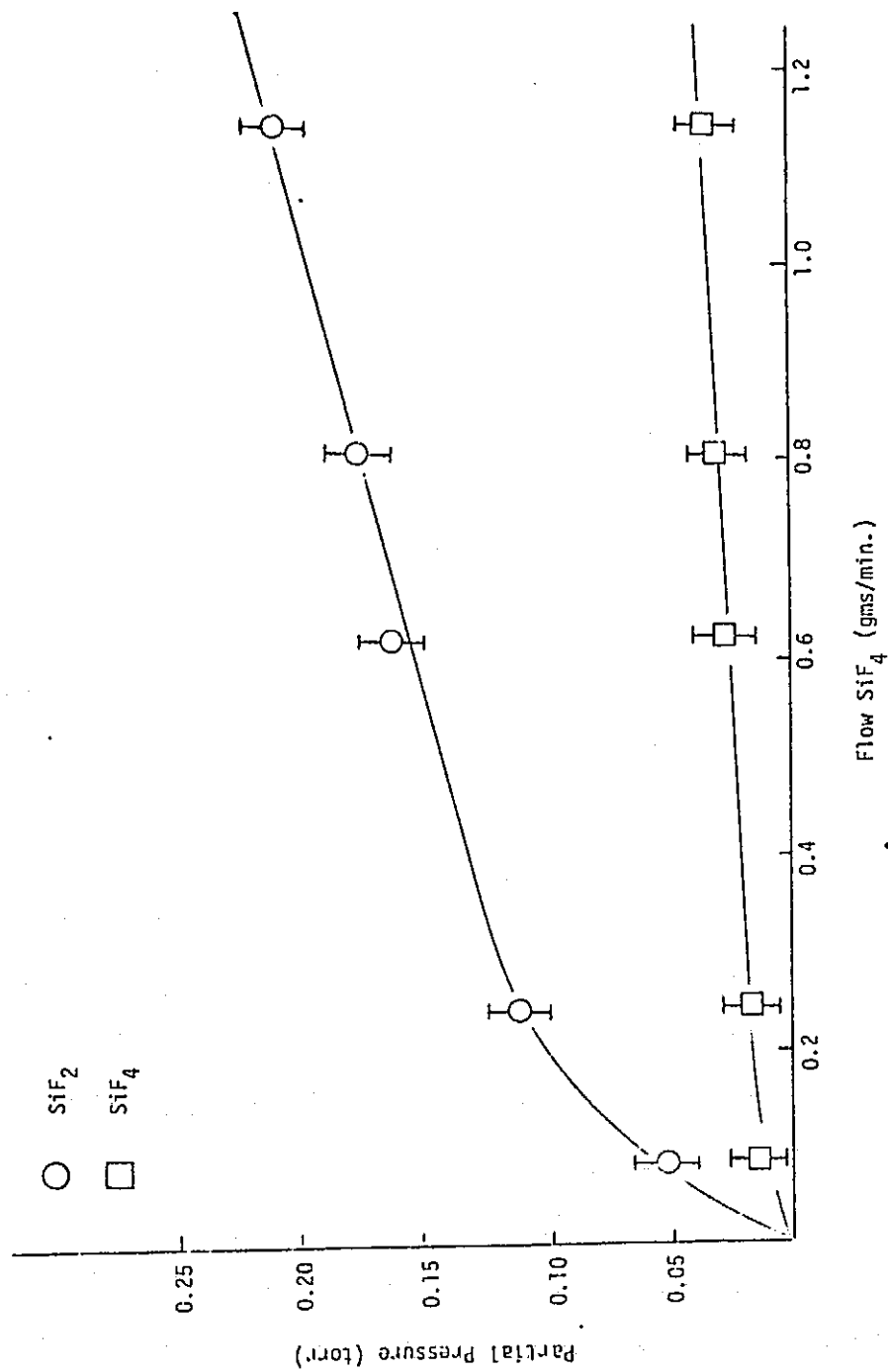


Figure 2. Partial pressure of  $\text{SiF}_4$  and  $\text{SiF}_2$  versus  $\text{SiF}_4$  flow for mg Si at  $1350^\circ\text{C}$ .

involved  $-100^{\circ}\text{C}$  condensation of  $(\text{SiF}_2)_x$  on the coil, and the third set consisted of condensation of  $(\text{SiF}_2)_x$  on the coil at temperatures between  $-70^{\circ}\text{C}$  and  $-35^{\circ}\text{C}$ . The polymer formed in these experiments was converted under the same conditions at temperatures between 0 and  $550^{\circ}\text{C}$ .

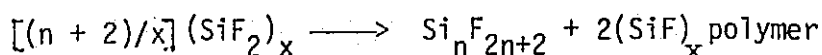
Regarding condensation temperature, a temperature of  $-69^{\circ}\text{C}$  was found to effectively condense the polymer on the first three coils of the quartz helix.

It is concluded that  $-69^{\circ}\text{C}$  is sufficient to trap gaseous  $\text{SiF}_2$  on the 36 inch C-D coil yet allow minimum  $\text{SiF}_4$  to co-condense with the polymer.

In our initial experiments, conversion of the polymer via reaction step 3 appears to follow the same sequence of steps for all three sets of experiments described above. Specifically, at temperatures of  $+170$  to  $200^{\circ}\text{C}$  oils appear at the interface of the polymer and the heated quartz spiral. The unconverted polymer is thus separated from the coil by these oils and falls under gravity to the bottom trap. (Figure 1a).

The polymer in the trap is heated between 0 and  $510^{\circ}\text{C}$  ( $\sim 10^{\circ}\text{C}/\text{minute}$ ) where it is observed that at  $250$ - $300^{\circ}\text{C}$  the polymer melts liberating oils and leaving a residue. Further heating results in a rapid formation of oils at approximately  $390^{\circ}\text{C}$ , followed by formation of silicon from the latter at  $410$ - $510^{\circ}\text{C}$ .

Margrave reports that at  $200$ - $350^{\circ}\text{C}$  the  $(\text{SiF}_2)_x$  decomposes to give perfluorosilanes,  $\text{Si}_n\text{F}_{2n+2}$  and leaves a silicon rich polymer.<sup>3</sup>



Further, he states that at  $400^{\circ}\text{C}$  the decomposition becomes very fast yielding mainly  $\text{SiF}_4$  and Si. These observations are consistent with ours;

in addition, we observed that the reaction at 400°C coincides with the formation of oils from the "silicon rich polymer."

It has been observed by us that the polymer conversion appears to involve initial formation of oils, followed by thermal disproportionation to Si. Mass spectral analysis of the  $\text{Si}_n\text{F}_{2n+2}$  fragments liberated upon heating of the polymer as listed in Table III together with the temperature at which they were observed.

TABLE III

Mass spectrum of volatile components  
of polymer thermal decomposition.

$\text{Si}_n\text{F}_{(2n+1)}$	m/e	T°C
$\text{Si}_2\text{F}_5^+$	151	180°C
$\text{Si}_3\text{F}_7^+$	217	285°C
$\text{Si}_4\text{F}_9^+$	283	Liberated from cold trap after passing 500°C quartz coil

Table III is not inclusive but does indicate that the lower molecular weight fragments are liberated in the initial heating stages.

In view of the apparent formation of oils from the polymer and subsequent thermal disproportionation reaction, effort has been directed toward high temperature (750°C - 950°C) disproportionation by passage of the oils past a hot zone or hot collar, located at the top of the trap (3 in Figure 1a). In this technique the volatile products of the oils generated at low temperatures  $\leq 400^\circ\text{C}$  are passed across a high temperature (750°C - 950°C) quartz hot zone where disproportionation into silicon occurs. Volatiles, not disproportionated, condense in a cool zone ( $>170^\circ\text{C}$ ) above



the hot collar, then pass back through the hot zone and disproportionate. They then liberate volatiles and/or condense into the bottom trap where they are again heated above their boiling point liberating the more volatile constituents. This reflux-disproportionation technique allows separation of volatile homologues as in a more conventional fractional distillation but offers the advantage that collection and subsequent disproportionation of the individual homologues is not required, because the separation of the homologues is affected by their disproportionation into silicon upon exposure to the high temperature zone.

Further, it is likely that with each pass of the hot zone, the number of components remaining in the homologue mixture is reduced as would occur in a conventional fractional distillation.

Experiments are being conducted to determine the residence times at various temperatures which will be necessary to convert the homologues into Si and  $\text{SiF}_4$ .

#### D. $\text{AlF}_3$ Mass Spectral Studies

A series of experiments was initiated to study the chemistry of the major impurities in the mg silicon charge under  $\text{SiF}_2$  transport reaction conditions. Of particular interest is the possible transport of Al as an aluminum fluoride. The overall Gibbs standard free energy of formation for the reaction between Al and  $\text{SiF}_4$  is negative.<sup>8</sup> In these experiments  $\text{AlF}_3$  was chosen as the transported impurity and the reaction monitored via the GC/MS data system.

$\text{AlF}_3$  (0.3 gm) was placed in a small quartz cup in a quartz furnace tube and connected directly to the Finnigan mass spectrometer (see Appendix I). The temperature of the  $\text{AlF}_3$  was increased during four hours, from ambient to approximately  $1150^\circ\text{C}$ , during which time mass spectra were recorded at 30 second intervals and at various electron ionization potentials (17-71 e.v.).

# ALF<sub>3</sub> NEAT SUBLIMATION

# 4

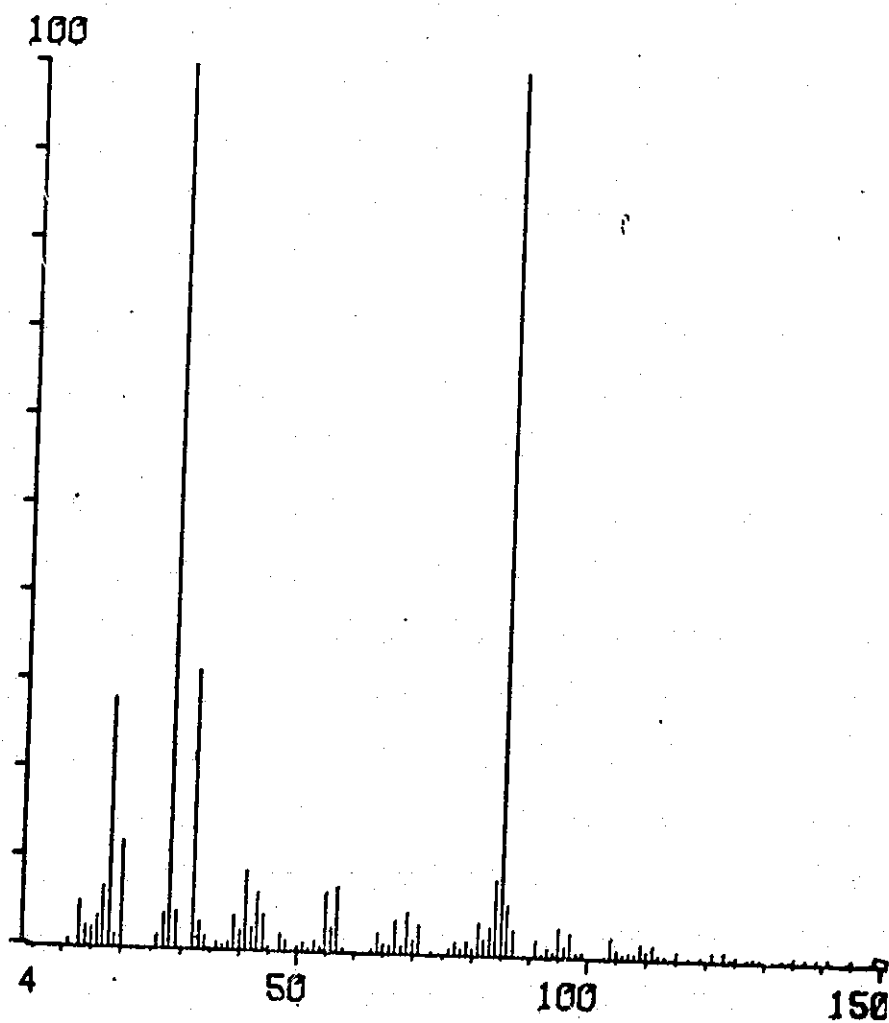


Figure 3. The mass spectrum above was obtained from AlF<sub>3</sub> sublimed through a quartz furnace tube (~650°C). Evidently the AlF<sub>3</sub> reacts with SiO<sub>2</sub> to form the SiF<sub>4</sub> observed. (See Table IV).

TABLE IV

Mass spectrum<sup>a,b</sup> of volatile components of  $\text{AlF}_3$  sublimation through a quartz furnace tube (see Figure 3).

<u>m/e</u>	<u>int(%)<sup>c</sup></u>	<u>Possible Assignment</u>
104	3	$\text{SiF}_4^+$
86	6	isotope of m/e = 85
85	100	$\text{SiF}_3^+$
84	8	$\text{AlF}_3^+$
57	7	U A <sup>d</sup>
55	6	U A
43	6	U A
41	9	U A
32	30	$\text{O}_2^+$
28	100	$\text{N}_2^+$

a. Normalized at m/e 85 = 100%.

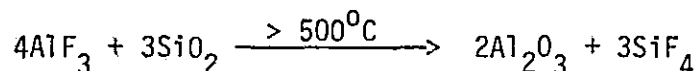
b. Obtained at 71 eV on Finnigan 3300 GC/MS.

c. Peaks with intensities less than 5% not included except m/e = 104.

d. U.A. = unassigned

Figure 3 contains a typical mass spectrum of the sublimed  $\text{AlF}_3$ . As can be seen in Table IV this is a typical spectrum of  $\text{SiF}_4$ , not  $\text{AlF}_3$ . This sublimation experiment was repeated as before with identical results, i.e., when  $\text{AlF}_3$  is sublimed through quartz tubing the only volatile component observed in large quantities is  $\text{SiF}_4$  not  $\text{AlF}_3$ .

This unexpected result could be explained by the following reaction:



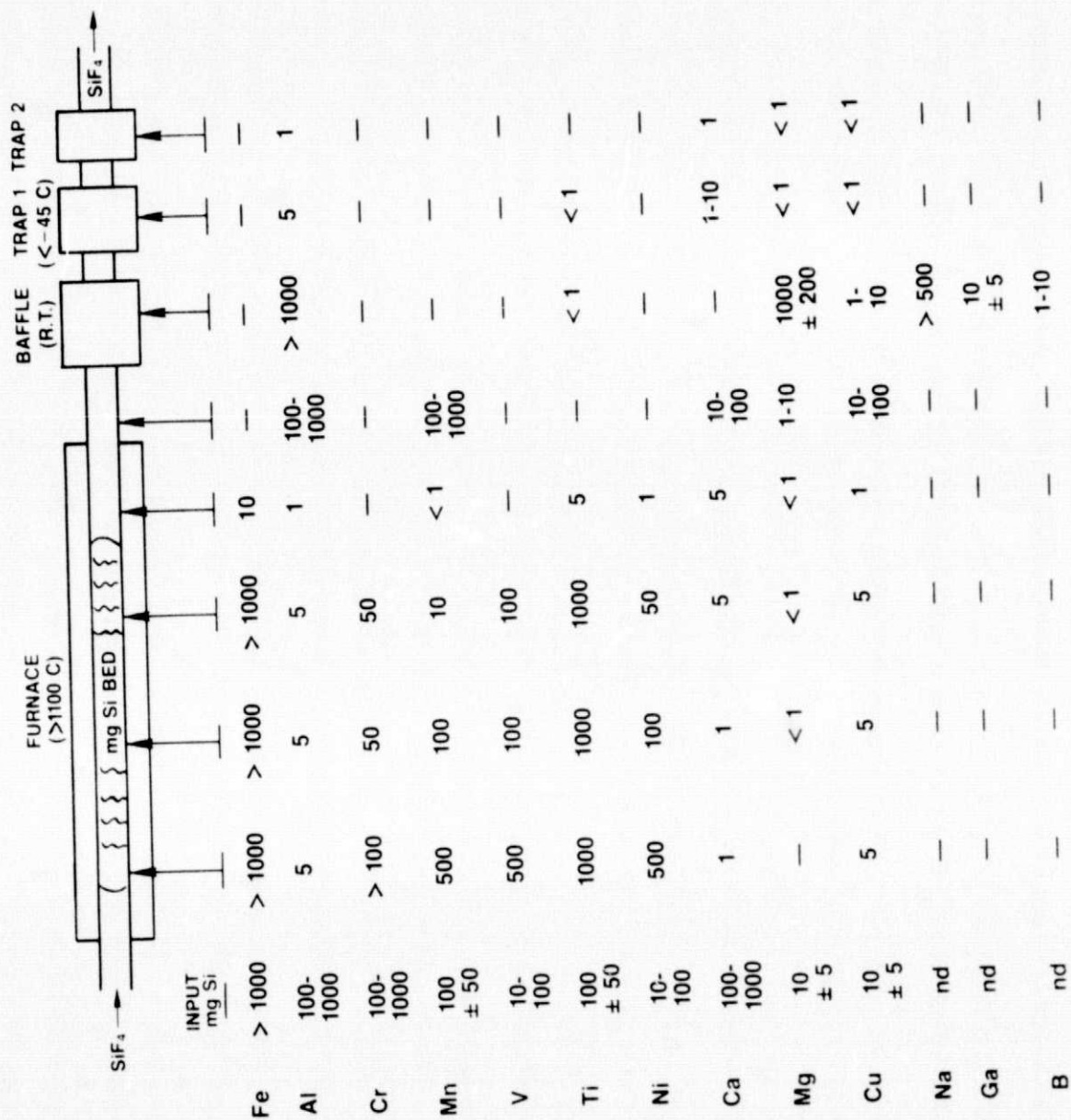
This reaction is similar to the reaction of Al with  $\text{SiO}_2$  which is utilized by the semiconductor industry to bond aluminum to  $\text{SiO}_2$  passivated silicon wafers.<sup>9</sup>

The reactions of Al and  $\text{AlF}_3$  with  $\text{SiO}_2$  to form inert and non-volatile  $\text{Al}_2\text{O}_3$  is likely one of the reasons why the Al impurity concentrations in the  $\text{SiF}_2$  polymer transport purification process have been reduced to where it approximated semiconductor grade when a quartz liner is used.

## E. Material Analysis

### 1. Impurity Balance Studies

Until the chemistry described in previous sections is more fully understood and the  $\text{SiF}_4$  recycling work is undertaken, it is not possible to do a complete impurity mass balance on the  $\text{SiF}_2$  polymer system. However, an incomplete balance based only on the solid deposits from various parts of the system can be useful and instructive. Figure 4 shows the results of a preliminary mass balance based on the emission spectroscopic analysis of samples taken from the system. The input material is typical mg silicon (Column 1). The next three samples were taken from the charge after a long series of runs reported in Quarterly Report #5. They were taken from locations in the charge as shown schematically in the figure. The next two samples



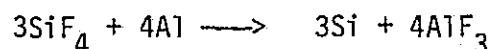
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Figure 4. Emission spec. results for samples taken from various sections of the  $\text{SiF}_2$  polymer transport system. All concentrations are in ppm wt.

are deposits formed in the furnace tube downstream from the hot zone. The baffle yielded the next sample. Samples number 69 and 68 are shown as the converted product formed from Traps 1 and 2 respectively.

From this data it can be seen where various impurities in the input charge material deposit. The three samples taken from the depleted charge itself show clearly that Fe, Cr, Mn, Ti, V and Ni are not transported to a large degree in the  $\text{SiF}_4$  gas stream. As the input gas stream impinges on the charge, Si reacts and is carried away leaving the impurities to build up in concentration. The data from the second and third sample show little impurity build up apparently because the gas mixture reached a steady state in the first section of the reactor. Another group of elemental impurities including Ca, Mg and Cu are present in low levels in the input charge and appear to be little changed at this stage of charge depletion.

Of particular interest is the rapid depletion of Al from the charge. We propose that metallic Al impurities react very rapidly with  $\text{SiF}_4$  to yield  $\text{AlF}_3$ , viz.,



Furthermore the mass spectral studies described in a previous section clearly indicate that once the Al has been volatilized as  $\text{AlF}_3$  it can undergo a reaction with the quartz liner to yield  $\text{Al}_2\text{O}_3$  and  $\text{SiF}_4$ . The major portion of the  $\text{Al}_2\text{O}_3$  remains as a coating on the quartz tube, but analysis of the deposits in the baffle also indicates that some is swept out of the tube and is trapped there.

This result indicates that a pretreatment of a fresh mg silicon charge with  $\text{SiF}_4$  may be an effective way to reduce Al content in the mg silicon charge. The gas would then be recycled. This is consistent with predictions made on the basis of freeenergy change ( $\Delta G$ ) for reaction of  $\text{SiF}_4$  with various impurities. Al and B are the only impurities of interest which have a negative  $\Delta G$ , thus these are the major ones expected to be transported.<sup>8</sup> In the case

of boron, it is present in such low levels in these samples that initial results do not clearly indicate the role boron is playing in the overall process.

The deposits between the hot zone and the product traps contain large amounts of impurities which form fluoride compounds of low and moderate volatility such as Al, Ca, Mn, Mg and Cu. No elements which form highly volatile fluorides deposit here.

The baffle is used to trap particulates and condense some polymer enhancing impurity nucleation from the gas stream. Three elements, Na, Ga and B were detected in this area which were not detected even in the input material. These elements could be present below ES detection limits in the charge and be concentrated in the baffle deposit underscoring the need for this stage in the apparatus.

The low level of impurities in the silicon produced has been discussed in previous reports.<sup>4</sup>

Recycling of the output gases will give information on the build up of highly volatile fluoride compounds in gas stream. One pass through the reactor does not permit build up to occur to the detection limits of GC/MS analysis. A complete impurity mass balance will be done during that phase of the program.

## 2. Crystal Growth from Product Silicon

Portions of the product produced from the long term, maximum rate engineering runs<sup>4</sup> were used for crystal growth\*. The results are tabulated in Table V. Runs 4-1, 4-5 and 4-6 were baseline experiments to verify that the furnace used did not contaminate the charge. The SiF<sub>2</sub> material used here was subjected to a high temperature final conversion to remove residual fluorides. The powder product was packed into a small crucible with a 60 g capacity for our Arthur D. Little HP crystal furnace for melting.

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\* It should be noted the crystal growth studies were conducted at Motorola's expense and are only described here to add clarity to the report.

TABLE V

Results for Crystal Growth Experiments  
for SiF<sub>2</sub> Transport<sup>0</sup> Silicon

<u>Run</u>	<u>Charge</u>	<u>Resulting Crystal</u>
4-1	52g of 7.6 $\Omega$ cm crystal P type	5.78 $\Omega$ cm P type 4.56 " "
4-5	50g 300 $\Omega$ cm N type poly	48.6 $\Omega$ cm N type
4-6	50g 300 $\Omega$ cm N type poly	958.2 $\Omega$ cm N type
4-7	9.9g SiF <sub>2</sub> product total conversion #3	N type - poly button
4-11	21.4g total conversion #3	Small button 0.11 $\Omega$ ohm N type
4-14	17.8g " " "	Not completely melted
4-15	17.8 " " #2	Button grown 0.11 $\Omega$ cm N type
4-22	40.4g from 4-7, 4-11, 4-14 and 4-15 etched charge	Crystal 0.10 $\Omega$ cm 4 pt probe N type 0.06 " spreading resist. probe
4-26	16.0g total conversion #2 10.0 " " #1 26.5 " " #3	Crystal 0.065 $\Omega$ cm 4 pt. probe N type



The powder is difficult to melt completely which was expected as RF heated furnaces, such as ours, do not efficiently melt powders. Resistance heated furnaces are more efficient, but none in the required size was available. In some cases, 4-7, 4-11 and 4-14, unmelted powder hindered direct crystal growth. In those cases the remaining melt was allowed to freeze, removed from the furnace and adhering pieces of the crucible were removed by etching in HF. The densified product was reloaded in the furnace for crystal growth (4-22). This process served to densify the  $\text{SiF}_2$  product for evaluation crystal growth. Since the entire charge was reloaded in this densification process no purification was expected due to segregation effects. In all cases the melts were extremely clean and no problems were encountered in crystal growth once melting was complete.

The resistivity readings indicate that the  $\text{SiF}_2$  product crystals contain 1.7 to 3.6 ppma of uncompensated phosphorus. This is the approximate concentration to be expected based on SSMS analysis of the product.

#### IV CONCLUSIONS AND RECOMMENDATIONS

During the early part of this quarter it was determined that the  $(\text{SiF}_2)_x$  polymer converted via  $\text{Si}_n\text{F}_{2n+2}$  homologues which could reduce conversion yields. Consequently, some of this quarters' goals were redefined while an investigation was undertaken to define the scope of the low conversion efficiency problem and propose a solution. The preliminary results of this investigation strongly suggest that the  $\text{Si}_n\text{F}_{2n+2}$  homologues can be converted into  $\text{SiF}_4$  and silicon in high yields in a continuous manner. Throughout the coming quarter we will continue to elucidate the chemistry of the  $(\text{SiF}_2)_x \longrightarrow \text{Si}_n\text{F}_{2n+2} \longrightarrow \text{Si} + \text{SiF}_4$  conversion. From our present knowledge and results of these studies, a conversion sequence will be defined and demonstrated which will yield sg silicon at high efficiencies and high rates. At the conclusion of these studies no obstacles were foreseen which would limit the feasibility of the process for low cost production sg silicon. Therefore it is recommended that the program be carried out as dictated by the Program Plan/Milestone Chart, leading to the significant conclusions and points of decision within the next quarter.

## V NEW TECHNOLOGY

There have been no reportable "New Technology" items uncovered during this reporting period.

## VI PLANS

Motorola's plans for the upcoming quarter entail:

1. Defining the parameters (temperature and residence times) for optimum conversion of the  $\text{Si}_n\text{F}_{2n+2}$  homologues into  $\text{SiF}_4$  and Si.
2. Re-examining the direct conversion of the polymer into  $\text{SiF}_4$  and Si.
3. Building a small prototype apparatus to demonstrate the feasibility of the conversion of  $\text{Si}_n\text{F}_{2n+2}$  homologues and  $(\text{SiF}_2)_x$  polymer into  $\text{SiF}_4$  and Si in high yields.
4. Complete construction of the large quartz coil, which will facilitate production of non-contaminated high purity silicon from the  $(\text{SiF}_2)_x$  polymer transport purification process.
5. Continuing work on mass balance and material analysis studies to demonstrate how the impurities in the mg silicon charge are removed, where they deposit and their role in the overall purification process.

## VII PROGRAM PLAN/MILESTONES

Status of the program is shown on the Program Plan/Milestone Chart, Figure 5.

TASK 1	SUB TASK NO.	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR
Dopant levels & atmos. effects	7														
Total Pressure & Particle pressure of SiF <sub>2</sub>	13														
TASK 2															
Analysis of Final Sample	35														
TASK 3															
Financial Mgmt Report	4	▲	▲	▲	▲	▲	▲								
NASA 533M															
Status & Cost Report	5	▲	▲	▲	▲	▲	▲								
Summary (JPL 3645)															
Status & Cost Report (JPL 3645-1)	6	▲	▲	▲	▲	▲	▲								
Technical Progress Reports	7	▲	▲	▲	▲										
Quarterly Reports	8		▲			▲									
Final Technical Report (draft)	10											▲			

PROGRAM PLAN/MILESTONE CHART

Figure 5

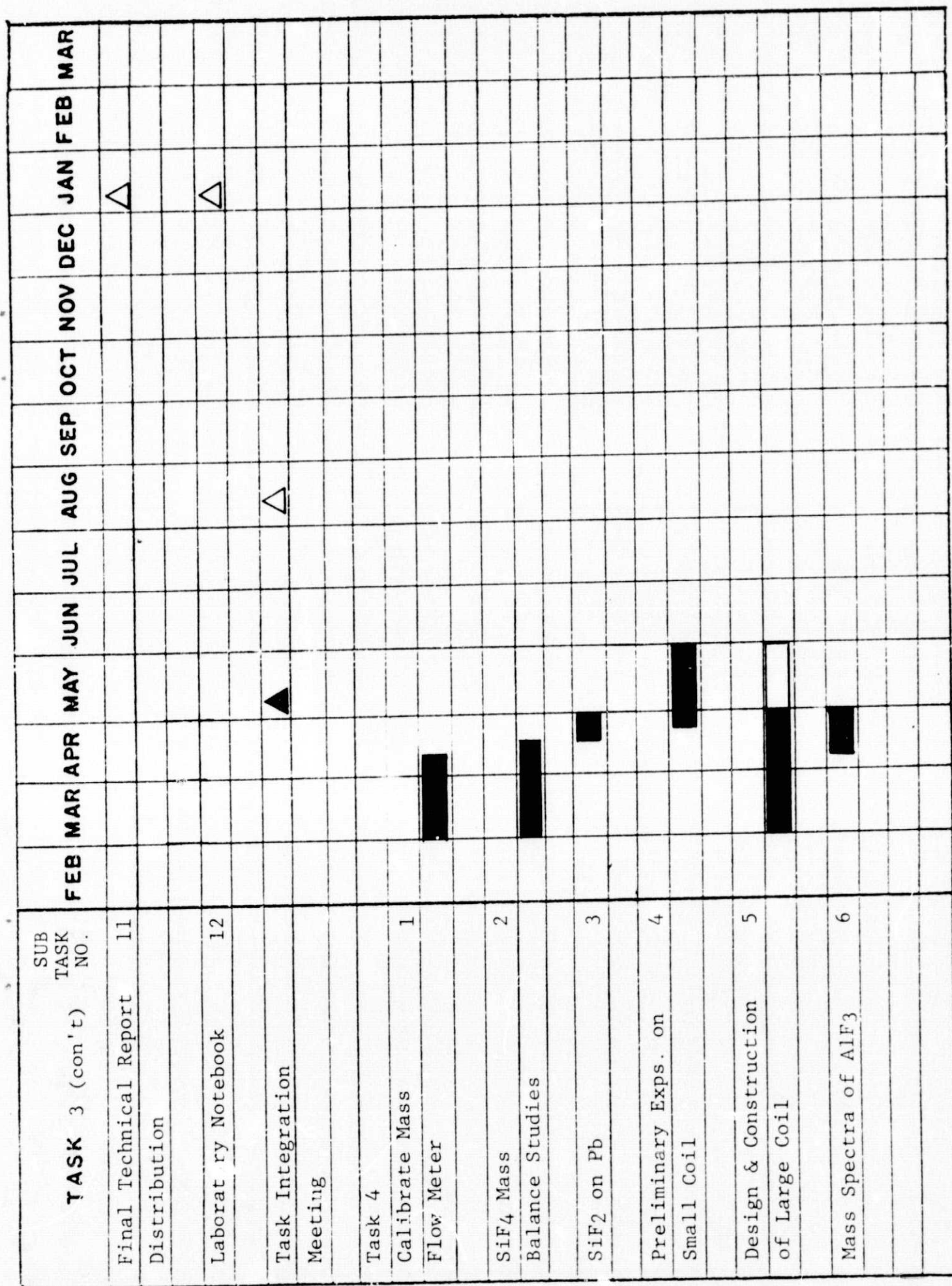


Figure 5

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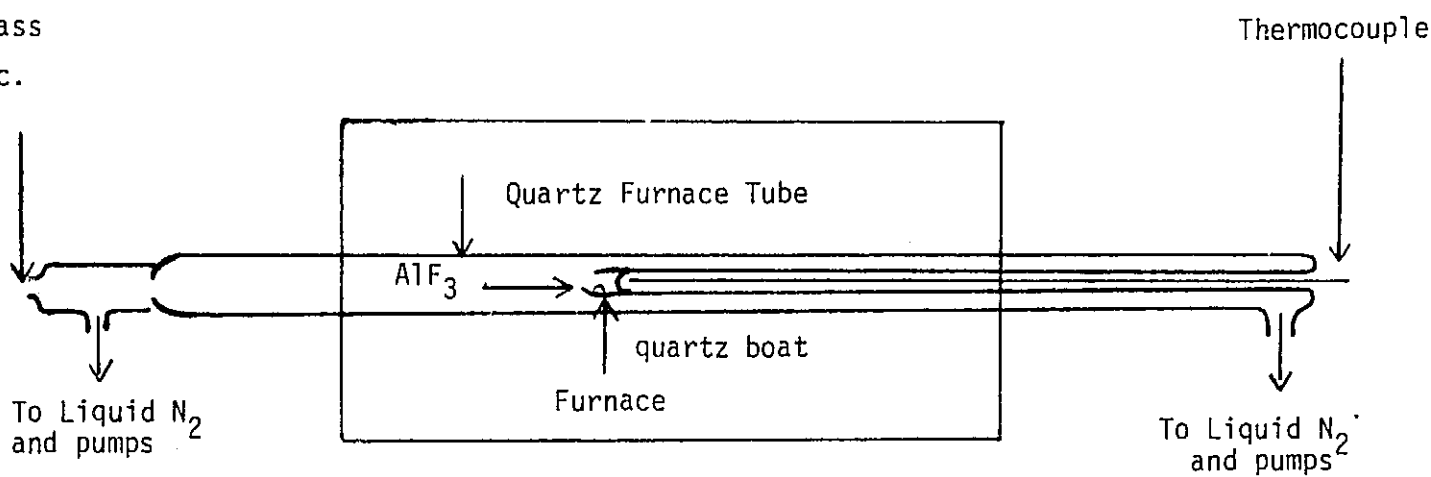
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## APPENDIX I



To Mass  
Spec.



The apparatus above was used to sublime the  $\text{AlF}_3$  directly into the e.i. source of the Finnigan mass spec. The only peaks observed arose from  $\text{SiF}_4$ , not  $\text{AlF}_3$ .

The following reaction was proposed to account for the unexpected observation

